JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 14 No 6, 06007(4pp) (2022)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 14 № 6, 06007(4cc) (2022)

Lead-Free Piezoelectric Materials for Medical Diligence

Gagan Anand*

Department of Physics, SOE, University of Petroleum and Energy Studies, 248007 Dehradun, India

(Received 13 October 2022; revised manuscript received 20 December 2022; published online 27 December 2022)

Piezoelectric-based transducers are comprehensively applied in biological treatments and cures. In this work, I would like to portray the chronicle and advancements of this. Parts of the human body like skin, bones, and blood cells exhibit piezoelectric property, as well as an inherent property, which helps disease treatment. The paper also discusses how piezoelectric materials can be utilized in medical implants, as sensors, and replace natural body parts. The review provides a better understanding of prospects and confronts regarding the future implementation of piezoelectric ceramics as a replacement for parts of the human body and its significance in the medical industry.

Keywords: Piezoelectric effect, Sensors, Transducers, Biological applications.

DOI: 10.21272/jnep.14(6).06007

PACS numbers: 77.65. – j, 07.07.Df, 07.10.Cm, 07.05.Pj

1. INTRODUCTION

1.1 Technology Development

Piezoelectric biotic sensors are extensively studied and reported in the literature such as bone piezo-sensors or biopolymers. In the present work, we try to explore a broader overview and implementations for the advancement of technology. Fukada showed that piezoelectricity was present in the vein, bone, muscles, ligaments, and intestines [1]. There have been several more studies since that time, which also contributed to the general understanding of the piezoelectric characteristics of the body, its origins, and how medical science should apply them. The human body's organic piezoelectric effects will make piezoelectricity a fundamental biological characteristic because most biological molecules are not symmetric. Most of the organs tend to move proteins as they pose piezoelectric properties. The indispensable building blocks of proteins present in homo sapiens are amino acids. As reported by Fukuda and researchers, these structures predominate over molecules such as elastin, collagen, and keratin and in the organs [2-5].

Pure amino acids with their own, because of the presence of polar-side dipoles, piezoelectric properties are seen in groups in Fig. 1. The piezoelectric property of macromolecules is due to the reorientation and transfer of biological dipole moments. At least fifteen piezoelectric properties are exhibited by amino acids, mainly the "L" form; γ-glycine, however, are present. One of the strongest piezoelectric amino acids is DL-alanine. Most ceramic mixtures or DL alanine, since their crystal types have a center of symmetric amino acids, do exhibit piezoelectric properties. The structure of amino acids is shown in Fig. 1. Medical piezoelectric devices and many biomedical piezoelectric uses are beyond the aforementioned aims of replicating or using biological piezoelectric phenomena.

In most applications, the choice of the sensor depends on the strength of the piezoelectric effect and financial requirements. Lead zirconium titanate (PZT) or quartz are the most commonly used materials in the industry. The primary reason is their cost-effectiveness, higher value of piezoelectric coupling coefficient, and the parameters can be modified with ease. But PZT is environ-mentally hazardous, so we recommend to use lead-free bismuth layered structured ferroelectric (BLSF) materials which are oxide center compounds operated at a wide range of temperatures. The development of implants or technologies that require direct human touch is more constrained. Since lead is not present in ceramics such as quartz, barium titanate, and sodium niobate potassium, they are well adapted biologically [4]. Furthermore, several biomedical doctors, due to the complex nature of instruments, require greater versatility than ceramics can offer. Bioattuned polymers are found in the majority of biological materials and PVDF copolymers. To date, PVDF polymer applications include, but are not limited to, biomechanical energy extraction systems, sensors, and wound scaffolds. Table 1 gives details of the piezoelectric properties of organs and their corresponding molecules.

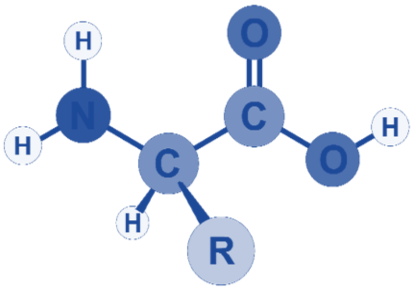

Fig. 1 – Structure of amino acid [6]

2. EXPERIMENT

2.1 Lead-Free Piezoelectric Materials: Preparation Technique

The following flow chart explains the preparation of bismuth layered perovskite ferroelectric (BLPF) materials. BLPF plays an enhanced function in comparison to PZT materials as lead is environmentally hazardous over SBT. The chemicals are taken as per the weight in an extreme pure 99.9 % form of sigma Aldrich make. They are mixed in a proper ratio as per the balancing conditions followed by grinding with mortar and pretzel

---

[*] ganand@ddn.upes.ac.in

for 4 h. Then the powder sample is subjected to calcination at 825 °C for 2 h. As the compounds are taken in the form of oxides and carbonates, the process of calcination will help remove carbon dioxide, leading to the formation of the balanced stoichiometry of the compound. Using the desired die of known diameter, the samples are pressed into pellets. The pellets are then sintered at 1200 °C to obtain the final densified samples [2, 3].

Material are precisely weighed based on the composition being fabricated as per stoichiometry.

Synthesized through solid-state reaction by ball or attrition milling a mixture of the oxides in isopropanol, to achieve a uniform particle size distribution

A magnetic stirrer or magnetic stir plate is commonly used in laboratories to ensure liquid samples are homogeneous in consistency. An inbuilt heater is used to evaporate the liquid, hence reduce the slurry.

The slurry is calcined in high-purity, refractory kiln furnace. Calcination is a process to remove carbon dioxide.

Dyeing leads to compact the material removing air gaps between particles. Improving the density of the martials

coalesce into a solid or porous mass by means of heating (and usually also compression) without liquefaction.

Fig. 2 – Flow chart: preparation of lead-free piezoelectric ceramics

2.2 Piezoelectric Sensors

Piezoelectric devices act as transducers converting mechanical energy into electrical one, hence can be used to produce and detect charge based on physical body movements. They can be extremely useful in identifying diseases and sometimes cure. They are especially important for the analysis of dynamics. Pressure changes, rhythmic movements such as pulse or heartbeat, and higher pressures (1 Pa-10 kPa) provide sound waves and tactile sensing. By structure or material, piezoelectric sensors offer a wide pressure range that meets standard requirements, so they are widely used as wearable devices or implants in biotic applications and become more user-friendly. The program examines the patient for early warning indicators that may have gone unnoticed between scheduled check-ups while wearing their device. A particular application is a synthetic skin for piezoelectric pressure sensing.

Like the minimum requirements, it is the amount of force, specific location of the touch, and above all the sensitivity factor of the skin that must be part of the synthetic skin. People have a wide range of mechanoreceptors with a frequency range of 0 to 0.5 kHz and a spatial resolution of less than 5 mm. It should also have thermal measurements. One of the sources of vibration sensors is the human skin, amplifying tactile stimuli. Transducers such as piezoelectric materials offer a solution for the measurement and positioning of contact forces. Polymer artificial skin is widely used due to its touch, feel, and adaptability to human skin. Polymers, such as fingerprints, can be sculpted to replicate human traits and increase their sensitivity. Electrospinning, for example, can be improved by aligning the dipoles of molecules. In an analogous technique, the use of composite materials or materials with higher piezoelectric properties can be achieved by structuring ceramics and polymers. Although there is a list of products that can be used for this tenacity, they are organized in ranks called arrays. An electrical signal is produced by a single unit in the array, indicating the array function. The electrical signal will arrive at a point in prosthetics where it can still detect tactile contact. Interference between signals, sometimes called Yeah, is one of the problems of arrays, along with intermodulation. During intermodulation, the unit experiencing force affects neighboring units, becomes activated, and starts to send signals of their own.

2.3 Organic Materials – Piezoelectricity

Organic materials possess low crystal symmetry. Hence the piezoelectric effect is due to the motion of dipoles in polymers. In recent years, silk and collagen are considered as most favorable piezoelectric materials [7]. Table 2 shows the piezoelectric coefficients for various piezoelectric materials classified as organic or inorganic. Because of its high piezoelectricity, remarkable chemical resistance, thermal stability, outstanding processability, and mechanical properties, polyvinylidene fluoride (PVDF) and its copolymers are the most researched piezoelectric materials. PVDF piezo-crystals are available in five phases, out of which the β-phase has excellent piezoelectric properties [8-10]. PVDF tends to show a dipole moment above zero [1, 11, 12] In some structures, dipole alignments are antiparallel, so that the total dipole moment is zero. Suitable examples are α PVDF piezo-crystals.

Polylactic acid (PLLA) exhibits lower d_{33} than inorganic ceramics like PZT but shows large piezoelectric shear constant due to the shape of the nanofilm. Depending on the stretching direction, a PLLA crystal can change from α to β-crystal based on the arrangement of dipoles [13]. PLLA is a compliant polymer and an excellent candidate for mobile device diligence [14].

Table 1 – Body organs and the corresponding molecules exhibiting piezoelectricity

Body organ	Molecules representing piezoelectric
Hair	Keratin
Lung tissue	Elastin
Skin (horny layer and epidermis)	Keratin
Breast nerves	Collagen
Bone	Collagen
Hair – surface	Prestin

Table 2 – Piezoelectric coupling coefficients for assorted piezoelectric materials

	Material	**Type**	**d_{33} (pC/N)**	**d_{31} (pC/N)**	**Refs**
Organic	PVDF	Polymer	– 33	23	[15]
	PLLA		6-12	–	[16]
Inorganic	AIN	Ceramic	3-6	– 2	[17]
	PZT-5H		593	– 274	[18]
	$BaTiO_3$		190	– 78	[19]
	$LiNbO_3$		16	– 1	[20]
	PMT-PT	Single crystal	2000-3000	–	[21]
	Quartz		2.3	– 0.67	[22]

2.4 Piezoelectric Biotic Balance

Piezoelectric sensors can be used in the detection of diseases or smell by exploiting the chemical properties of the sensors. A piezoelectric biotic balance can be used for a range of applications in compositional analysis and gas leakage detection. The density and viscosity of the liquid can be determined with 99.99 % accuracy. This technique is based on changes in mass in a crystal-covering film. In general, the 5-10 MHz range of quartz microbalances works; the Sauerbrey equation measures the accumulation of mass. Biotic molecules embedded in piezoelectric materials are used as sensors. The quartz vibration frequency is a function of mass, as mass varies, the vibration frequency changes. As mass increases beyond the threshold, the results are inaccurate, so a more precise estimate in the form of a sensor is required.

2.5 Energy Harvesting

They require a handy supply of energy to have implanted sensors inside the body. If the sensor is powered by a battery, removing and repairing it would necessitate additional surgery. In the case of the pacemaker, the main aim is to restrict the count of sensors to be installed in the body during surgery. The charge storage issues in the case of pacemakers can be eliminated using piezoelectric energy harvesting devices, which are capable of producing charges using body movements and can be used as integration or replacement of batteries.

Special attention and accuracy are required to reap energy from the organs. Biocompatibility should be one of the keys to this. The energy harvesting system should not contain toxic elements like lead, etc.

One of the most essential areas for power generation using piezoelectric sensors is a vibrating cantilever, which is needed to be embedded with biotic molecules. A typical structure of energy harvesting sensors is shown in Fig. 3. The outer layer is a molecular sensor inside which we have a silicon soft layer that will support the physical strength of the sensor followed by the piezo sensor. The terminals shown can be connected with the implant devices or the wearable. In this case, lead-free piezoelectric devices do a quantum of work.

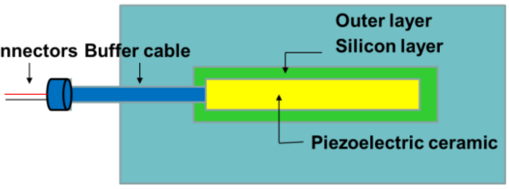

Fig. 3 – Piezoelectric energy harvesting sensor

3. CONCLUSIONS

The purpose of this paper was to show an outline of the biomedical piezoelectric productiveness. We talked about the piezoelectric characteristics of biotic materials and prospective applications. They might be utilized to cure diseases. Piezoelectric materials are also used in sensors and other devices. There are huge opportunities for research, development and implementation in the fields of human biological devices and in the medical industry, and they have impeachable scope for inevitable development.

ACKNOWLEDGEMENTS

Support from the Central Instrumentation Center (CIC) of the University of Petroleum & Energy Studies (UPES), Dehradun, India, is gratefully acknowledged.

REFERENCES

1. E. Fukada, *Ultrasonics* **6** No 4, 229 (1968).
2. G. Anand, P. Kuchhal, P. Sarah, *Partic. Sci. Technol.* **33** No 1, 41 (2015).
3. G. Anand, A.R. James, T.R. Krishna, P. Sarah, *Defence Sci. J.* **57** No 1, 1 (2007).
4. J. Dargahi, *Sensor. Actuat. A: Phys.* **80** No 1, 23 (2000).
5. Jaesung Yoon, Sangjoon Kim, Dongjin Kim, Il-Doo Kim, Seungbum Hong, Kwangsoo No, *Small* **11** No 31, 3750 (2015).
6. Y. Zang, F. Zhang, C. Di, D. Zhu, *Mater. Horiz.* **2** No 2, 140 (2015).
7. T. Furukawa, *IEEE Trans. Electrical Insulation* **24** No 3, 375 (1989).
8. P. Sajkiewicz, *Eur. Polym. J.* **35** No 9, 1581 (1999).
9. A. Gradys, P. Sajkiewicz, S. Adamovsky, A. Minakov, C. Schick, *Thermochimica Acta*, **461** No 1, 153 (2007).
10. L. Ruan, X. Yao, Y. Chang, L. Zhou, G. Qin, X. Zhang, *Polymers* **10** No 3, 3 (2018).
11. J.C. Anderson, C. Eriksson, *Nature*, **227** No 5257, 5257 (1970).
12. D. Puppi, F. Chiellini, A.M. Piras, E. Chiellini, *Prog. Polym. Sci.* **35** No 4, 403 (2010).
13. A.M.M.K. Shahin, *Energy conversion through local piezoelectric effect in polymer foams for enhancing sound absorption* (Doctoral thesis, Nanyang Technological University, Singapore) (2019).
14. T. Yoshida et al., *Jpn. J. Appl. Phys.* **49** No 9S, 09MC11 (2010).
15. Y.R. Jeong, S.Y. Oh, J.W. Kim, S.W. Jin, J.S. Ha, *Chem.*

Eng. J. **384**, 123336 (2020).

16. Y. Tajitsu, *IEEE Trans. Ultrasonics, Ferroelectrics, Frequency Control*, **55** No 5, 1000 (2008).
17. Y. Liu, Y. Cai, Y. Zhang, A. Tovstopyat, S. Liu, C. Sun, *Micromachines* **11** No 7, 7 (2020).
18. V.S. Bystrov et al., *Piezoelectric Nanomaterials for Biomedical Applications* (Eds. by G. Ciofani, A. Menciassi) (Berlin, Heidelberg: Springer: 2012).
19. F. Eskandari, M. Shafieian, M.M. Aghdam, K. Laksari, *Ann. Biomed. Eng.* **49** No 3, 991 (2021).
20. H.-K. Chang, C.-W. Huang, C.-C. Chiu, H.-J. Wang, P.-Y. Chen, *Macromolecules* **53** No 20, 8809 (2020).
21. J. Zhang, *Nano Energy* **79**, 105489 (2021).
22. R.E. Newnham, *Properties of Materials: Anisotropy, Symmetry, Structure* (Oxford: Oxford University Press: 2004).

Безсвинцеві п’єзоелектричні матеріали для медичної роботи

Gagan Anand

Department of Physics, SOE, University of Petroleum and Energy Studies, 248007 Dehradun, India

П'єзоелектричні перетворювачі широко застосовуються в біологічному лікуванні та терапії. У роботі я хотів би зобразити хроніку та досягнення цього. Частини людського тіла, такі як шкіра, кістки та клітини крові, мають п'єзоелектричні властивості, а також внутрішню властивість, яка допомагає лікувати захворювання. У статті також обговорюється, як п'єзоелектричні матеріали можна використовувати в медичних імплантатах як датчики та замінювати природні частини тіла. Огляд забезпечує краще розуміння перспектив і протистоянь щодо майбутнього впровадження п'єзоелектричної кераміки як заміни частин людського тіла та її значення в медичній промисловості.

Ключові слова: П'єзоелектричний ефект, Сенсори, Перетворювачі, Біологічні застосування.